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GB 0815154 A EP 0716090 A1 WO 95/32791 A1
US 5589050 A US 5135622 A US 4636296 A

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(54) Electrodialysis using ion-depleted water

(57) Electrodialysis is characterised by contacting the water to be purified with the anode and/or cathode, such that gas generated at the anode and/or cathode enters the impure water, using a portion of the ion-depleted water to supply the concentrating path, and concentrating gas present in the ion-depleted water in that portion which is supplied to the concentrating stream, thereby to diminish the concentration of gas in the reminder of the ion depleted water that is delivered as product. This portion is supplied by inlet 52 whilst purified water is dispensed at 64.

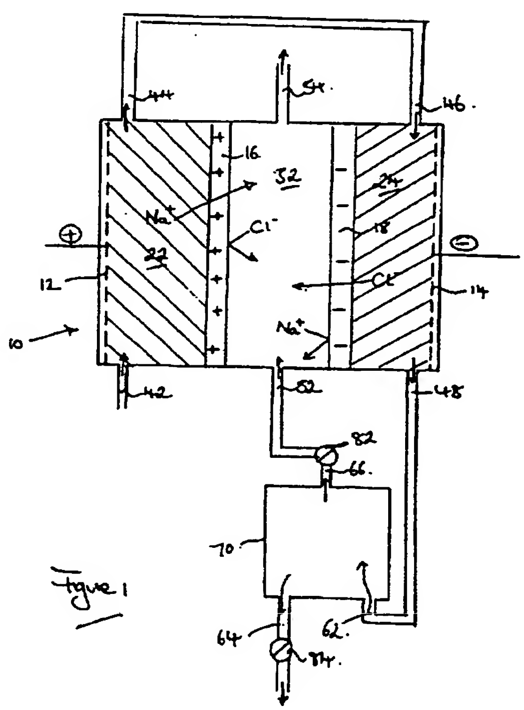

Figure 1

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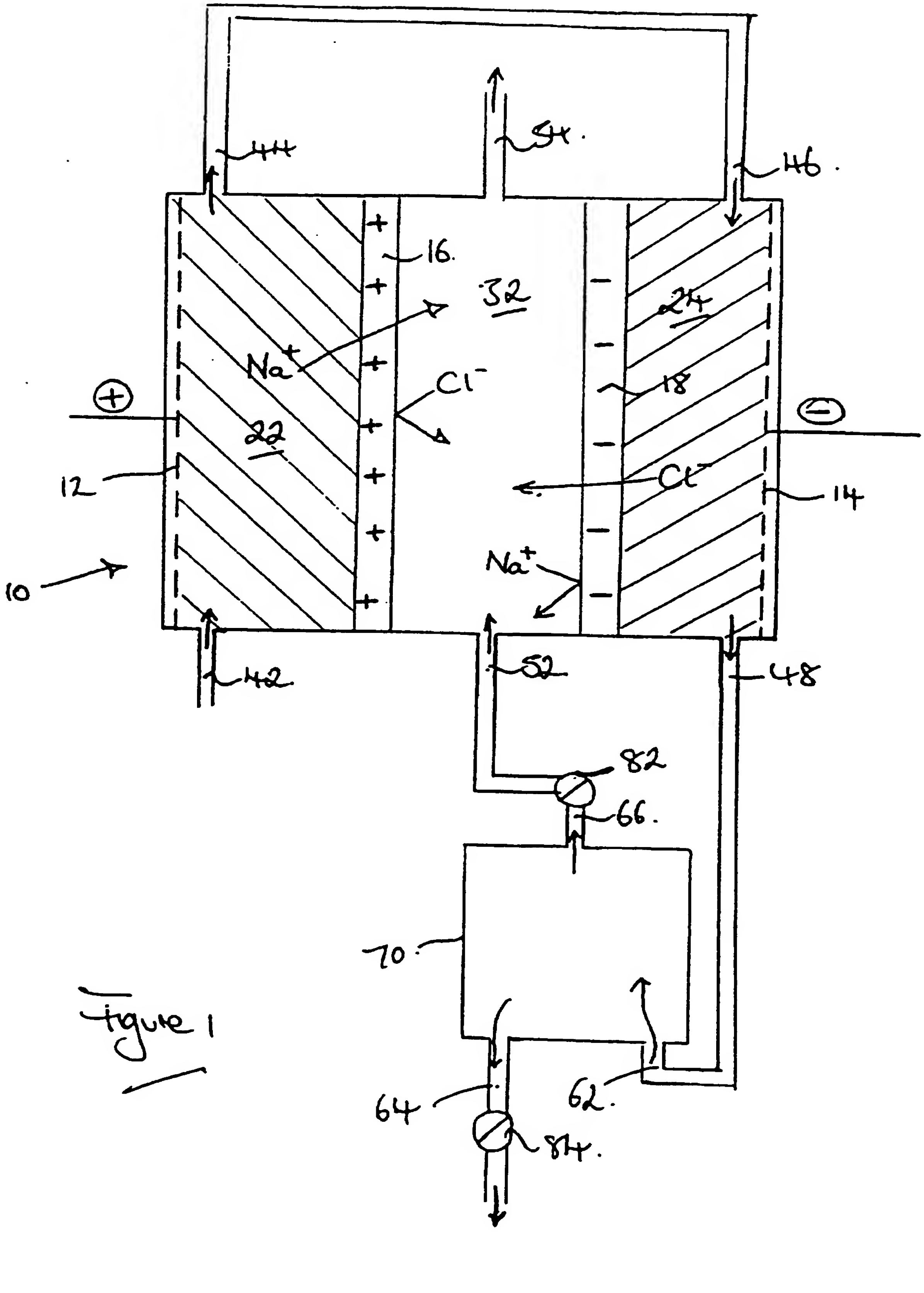

Figure 1

APPARATUS AND METHOD OF ELECTRODIALYSIS

The present invention relates to an apparatus for and method of electrodialysis which comprises removing ionic impurities from water to an acceptor liquid through a perm-selective membrane such for example as an ion exchange membrane under the influence of an electromotive force.

A method of electrodialysis is disclosed in GB-A-764067 to the Permutit Company Ltd. The method according to this disclosure comprises causing or allowing the impure water to move along a deionising path interjacent an anode and a cathode, causing or allowing a second acceptor liquid to move along an ion concentrating path in juxtaposition with the deionising path, which concentrating path is separated from the deionising path by a cation perm-selective membrane between the concentrating path and the anode and/or an anion perm-selective membrane between the concentrating path and the cathode, which second liquid is capable of receiving the ionic impurities from the impure water, and applying a potential difference between the anode and cathode, thereby to cause or allow anions in the impure water to enter the second liquid through an anion exchange

membrane and/or cations to enter the second liquid via a cation exchange membrane, thereby to remove the ionic impurities from the impure water.

It will be well known to a person skilled in the art that the deionising path at least may contain an ion exchange material such, for example, as ion exchange resin which is typically provided in the form of beads. Electrodialysis depends on there being a continuous electrolyte between the anode and cathode, and where water of a very high purity is required, electrodialysis becomes inefficient because the conductivity of the ion-depleted water in the deionising path presents a very high resistance to the applied electromotive force. The inclusion of an ion exchange material in the deionising path serves to maintain a conductive "bridge" across the deionising path between the anode and cathode even where the water therein has a very low ion content. It is well known that the ion exchange material may be solely cation or anion exchange material. Alternatively, a homogenous mixed bed or layers of cation and anion exchange material may be used. Electrodialysis using ion exchange material in the deionising path is sometimes known in the art as electrodeionisation. Examples of electrodeionisation methods are described GB-A-815154 and GB-A-877239 of the Permutit Company Ltd.

An improved electrodeionisation method is disclosed by Forschungszentrum Julich GmbH in their international patent application no. PCT/DE95/00696. This reference discloses an electrodeionisation apparatus comprising three compartments interjacent the anode and cathode. The compartments are defined by two spaced perm-selective membranes: a first anion perm-selective membrane is disposed at a position spaced from the cathode, and a second cation perm-selective membrane is disposed intermediate the anion perm-selective membrane and the anode. The two perm-selective membranes thus define a central compartment which forms the concentrating path and two spaced end compartments which contain the electrodes. The two end compartments together form the deionising path, and in service impure water is caused to flow through the two end compartments in succession. The water to be purified thus contacts the electrodes during its passage through the end compartments.

In use, when an electromotive force is applied between the anode and cathode, cationic impurities in the water are caused or allowed to migrate into the second liquid in the central concentrating compartment through the cation exchange membrane, and anionic impurities are caused to migrate into central compartment through the anion exchange membrane. The end compartments contain

ion exchange material and optionally the central concentrating compartment also contains ion exchange material. As discussed above, the ion exchange material in these compartments assists in maintaining a conductive path of low resistance between the two electrodes, thereby enabling the production of high purity water without requiring the application of an unduly high potential difference across the electrodes.

Persons skilled in the art will also appreciate that water-splitting will take place at the electrodes. In particular, hydronium ions will be produced at the anode, and hydroxyl ions at the cathode. This is advantageous, as these species regenerate the ion exchange materials in the end compartments.

In each compartment, said ion exchange material will typically comprise a bed of ion exchange resin beads, which bed may be compressed in order to increase the electrical conductivity of the bed. Preferably the bed(s) may be compacted by compression such as to improve the electrical efficiency of electrodeionisation, without damaging the resin beads, and without increasing unduly the hydraulic resistance of the bed(s). Pressures of up to about 500psi (3.45MPa) are envisaged.

A further advantage inherent in the method disclosed by application no. PCT/DE95/00696 is that oxidative gases produced at the anode will have a disinfecting effect on the water to be purified.

Disadvantages of the method disclosed by application no. PCT/DE95/00696 are that unwanted gases, particularly oxygen and hydrogen, are discharged into the deionising stream. Furthermore, whilst the disinfecting effect of oxidative gas in the deionising stream is an advantage, its presence in the final product is a disadvantage.

Electrodialysis methods of the kind described above are referred to hereinafter as methods of the kind described.

It is an object of the present invention to provide an electrodialysis method and apparatus which is capable of producing water of a higher ionic purity as compared with the methods of the kind described. It is also an object of the invention to provide an electrodialysis method which benefits from the advantages of discharging electrode gases into the water to be purified without producing product water which has a high gas content.

According to one aspect of the present invention therefore there is provided a method of the kind

described characterised by contacting the water to be purified with the anode or cathode such that gas generated at the anode or cathode enters the impure water, using a portion of the ion-depleted water as the second liquid in the concentrating path, and concentrating gas present in the ion-depleted water in that portion which is supplied to the concentrating stream, thereby to diminish the concentration of gas in the remainder of the ion-depleted water which is delivered as product.

The use of a portion of the ion depleted water to supply the concentrating path has the advantage of reducing the back-diffusion of ions from the concentrating path into the deionising path. In accordance with the present invention therefore this leads to a product water of low ionic content as compared with the methods of the kind described. Furthermore, as the electrode gases dissolved in the ion depleted water are concentrated in the portion of the ion depleted water which is returned to the concentrating stream, there is no need for additional gas separation techniques and the volume of ion-depleted water which is used for this purpose is minimised. Hence the amount of product water is maximised. The portion of the ion-depleted water which is used to supply the concentrating path may comprise 40 to 80% gas, typically

about 60%.

Yet another advantage of the present invention is that by concentrating the electrode gases in the portion of ion depleted water used as concentrating stream, the remainder of the ion depleted water which is used as product has a lower gas content.

Typically the deionising path may contain ion exchange material such for example as ion exchange resin beads. The production of hydroxyl and hydronium ions at the electrodes in the deionising path may therefore serve to regenerate continuously this ion exchange material.

In some embodiments the step of concentrating the gas in the portion of ion depleted water used in the concentrating path may comprise delivering the ion depleted water to a plenum receptacle in which the water is caused or allowed to stand prior to delivery as product, so as to allow gas present in the water to collect towards the top of the receptacle, and the portion of ion depleted water used as a second liquid in the concentrating path may be supplied from at or towards the top of the plenum receptacle where the water has a high gas content.

The water to be purified may be caused or allowed to move along the deionising path at a rate of about 2 to 10,000 litres per hour, and the second liquid may be caused or allowed to move through the concentrating path a low fraction of the overall flow, typically but not limited to 2 to 10%.

In a particular aspect of the present invention, the water to be purified may be subjected to a pre-purification step of reverse osmosis prior to admission in the deionising path.

In yet another aspect of the present invention there is provided an electrodialysis apparatus for removing ions as impurities from water, said apparatus comprising an anode and cathode, and means defining a deionising path for conducting the impure water interjacent the anode and cathode and a concentrating path for a second liquid juxtaposed the deionising path, which second liquid is capable of receiving ionic impurities from the impure water, wherein said means defining the deionising and concentrating paths comprises an anion perm-selective membrane which separates the concentrating and deionising paths from each other and disposed between the concentrating path and the cathode, or a cation perm-selective membrane which separates the concentrating and

deionising paths from each other and disposed between the concentration path and the anode, such that when a potential difference is applied between the anode and cathode in service, anions in the impure water are caused or allowed to migrate into the second liquid via said anion perm-selective membrane, or cations in the impure water are caused or allowed to enter the second liquid via the cation perm-selective membrane, thereby to deplete the impure water of ionic impurities; characterised in that the deionising path is arranged such that the impure water or partially purified water contacts the anode or cathode, such that the gas produced at the anode or cathode enters the partially purified water, supplying means are provided for supplying a portion of the ion depleted water as the second liquid to the concentrating path, and gas concentrating means are provided for concentrating gas in the ion depleted water in that portion of the ion depleted water that is supplied as second liquid, such that gas is depleted from the remainder of the ion depleted water which is supplied as product.

Said defining means may define two spaced deionising compartments which contain the electrodes, and a single concentrating compartment interjacent the deionising compartments. The deionising compartments may contain

ion exchange material, and the water to be purified may be caused or allowed to flow through the deionising compartments in succession. Optionally, the concentrating compartment may also contain ion exchange material.

Following is a description by way of example only with reference to the accompanying drawings of methods and apparatus for the carrying the present invention into effect.

In the drawings the Figure shows a schematic side view, partly in section, of an electrodeionisation apparatus in accordance with the present invention.

The electrodeionisation apparatus shown in the Figure comprises a cell (10) which comprises two spaced electrodes - an anode (12) and a cathode (14). Intermediate the anode (12) and cathode (14), two spaced perm-selective membranes sub-divide the cell (10) into three compartments. One of the perm-selective membranes, a cation permeable exchange membrane (16), defines a first diluting compartment (22) intermediate the anode (12). The other perm-selective membrane, an anion permeable exchange membrane (18), defines a second diluting compartment (24) intermediate the cathode (14). Intermediate the cation and anion exchange membranes

(16,18), the two membranes define a concentrating compartment (32).

Each of the three compartments is provided with a water inlet and an outlet. The inlet (42) to the first diluting compartment (22) is adapted for connection to a supply of water which is to be purified. The outlet (44) to the first diluting compartment (22) is connected to the inlet (46) to the second diluting compartment (24). The outlet (48) of the second diluting compartment (24) is connected to an inlet (62) in the bottom or towards the bottom of a plenum chamber (70). Said plenum chamber (70) is also equipped with a plenum outlet (64) at or towards the bottom of the chamber and a return conduit (66) which is connected to the inlet (52) to the central concentrating compartment (32). The outlet (54) of the concentrating compartment (32) is connected to a waste disposal system e.g. a sewer.

Each of the first and second diluting compartments (22,24) is filled with a bed of ion exchange resin beads. Typically, cation exchange resin beads may be used in the first diluting compartment (22), and anion exchange resin beads may be used in the second diluting compartment (24). Alternatively each of the first and second diluting compartments (22,24) may contain a mixed bed of

cation and anion exchange resin beads or alternate layers of cation and anion exchange resin. Suitable cation and anion exchange resins are commercially available at the time of writing and are well known to persons skilled in the art, as are suitable cation and anion permeable exchange membranes.

In service, water to be purified is inletted to the cell (10) via inlet (42) to the first diluting compartment and is caused or allowed to flow in succession through the first and second diluting compartments (22,24), and thereafter into the plenum chamber (70). Prior to admission to the first diluting compartment (22), the water to be purified may be subjected to a reverse osmosis pre-treatment.

During start-up, the plenum chamber will then fill progressively with water. The return conduit (66) and plenum outlet (64) are equipped with flow regulators (82,84). The regulators (82,84) and the flow rate inletted to the first diluting compartment (22) are controlled so as to provide a flow rate of about 20 to 100 litres per hour through the first and second dilution compartments and 1 to 10 litres per hour through the returning conduit (66). The water in the returning conduit (66) is admitted to the concentrating compartment

(32) via inlet (52) and is disposed of to waste through outlet (54).

Said concentrating compartment (32) may optionally be filled with a bed of ion exchange resin beads, which beads may comprise a mixture of cation and anion exchange resin beads, or may be solely cation exchange resin or anion exchange resin.

A potential difference is applied between the anode (12) and cathode (14), so as to cause migration of cations in the first diluting compartment through the cation exchange membrane (16) into the central concentrating compartment (32), and similarly migration of anions in the second diluting compartment through the anion exchange membrane (18) and into the concentrating compartment (32), thereby to deionise the water flowing through the diluting compartments (22,24).

Owing to reactions taking place at the electrodes (12,14), gas will be discharged into the diluting compartments. This gas will consist of hydrogen and oxygen in the main. Oxidative gases will have a disinfecting effect on any microbes in the water to be purified. Hydroxyl and hydronium ions will also be produced at the electrodes which ions will have the

advantageous effect of regenerating the ion exchange materials in the diluting compartments (22, 24).

During the residence of the water in the plenum chamber (70), the gas in the water will "settle" towards the top of the chamber (70) and will be admitted to the concentrating chamber (32) via the return conduit (66) with the returned purified water. The water returned to the concentrating chamber may contain 20-80% gas, preferably 40-70%, and typically about 65%. Conversely the remainder of the deionised water in the plenum chamber (70) will be depleted of gas, thereby improving the quality of the product water.

The use of desalted water in the concentrating compartment has the advantage of reducing back-diffusion of ions from the concentrating chamber (32) into the first and second diluting compartments (22,24) resulting in purer product water.

Product purified water may be dispensed via the plenum outlet (64).

It will be appreciated that alternatively, the apparatus can be operated with the water to be purified passing first through the second diluting compartment (24) across

the cathode, and thereafter through the first compartment (22) across the anode (22), with the plenum chamber (70) being connected after the first compartment (22).

CLAIMS

1. A method of electrodialysis comprising causing or allowing impure water to move along a deionising path interjacent an anode and a cathode, causing or allowing a second acceptor liquid to move along an ion concentrating path in juxtaposition with the deionising path, which concentrating path is separated from the deionising path by a cation perm-selective membrane between the concentrating path and the anode and/or an anion perm-selective membrane between the concentrating path and the cathode, which second liquid is capable of receiving ionic impurities from the impure water, and applying a potential difference between the anode and cathode, thereby to cause or allow ions in the impure water to enter the second liquid through an anion exchange membrane and/or cations to enter the second liquid via a cation exchange membrane, thereby to remove the ionic impurities from the impure water, characterised by contacting the water to be purified with the anode or cathode, such that gas generated at the anode or cathode enters the impure water, using a portion of the ion-depleted water as the second liquid in the concentrating path, and concentrating gas present in the ion-depleted water in that portion which is supplied to the

concentrating stream, thereby to diminish the concentration of gas in the remainder of the ion-depleted water which is delivered as product.

2. A method as claimed in claim 1 characterised in that the portion of the ion-depleted water that is used to supply the concentrating path comprises 40 to 80% gas, preferably about 60% gas.

3. A method as claimed in claim 1 or claim 2, characterised in that the step of concentrating the gas in the portion of the ion-depleted water used in the concentrating path comprises delivering the ion-depleted water to a plenum receptacle in which the water is caused or allowed to stand prior to delivery as product, so as to allow gas present in the water to collect towards the top of the receptacle, and the portion of ion-depleted water used as second liquid in the concentrating path is supplied from at or towards the top of the plenum receptacle where the water has a higher gas content.

4. A method as claimed in any of claims 1 to 3, characterised in that the water to be purified is subjected to a pre-purification step of reverse osmosis prior to admission in the deionising path.

5. An electrodialysis apparatus for removing ions as impurities from water, said apparatus comprising an anode and cathode; and means defining a deionising path for conducting the impure water interjacent the anode and cathode and a concentrating path for a second liquid juxtaposed the deionising path; which second liquid is capable of receiving ionic impurities from the impure water; wherein said means defining the deionising and concentrating paths comprises an anion perm-selective membrane that separates the concentrating and deionising paths from each other and is disposed between the concentrating path and cathode, and/or a cation perm-selective membrane that separates the concentrating and deionising paths from each other and is disposed between the concentration path and the anode; the arrangement being such that when a potential difference is applied between the anode and cathode in anions in the impure water are caused or allowed to migrate into the second liquid via a anion perm-selective membrane, and/or cations in the impure water are caused or allowed to enter the second liquid via a cation perm-selective membrane, thereby to deplete the impure water of ionic purities; characterised in that the deionising path is arranged such that the impure water contacts the anode and/or cathode, such that the gas produced at the anode or cathode enters the impure water, supply means are

provided for supplying a portion of the ion-depleted water as the second liquid to the concentrating path, and gas concentrating means are provided for concentrating gas in the ion-depleted water in that portion of the ion depleted water that is supplied a second liquid, such that gas is depleted from the reminder of the ion depleted water which is supplied as product.

6. An electrodialysis apparatus as claimed in claim 5, characterised in that said defining means defines two spaced deionising compartments which contain the electrodes, and a single concentrating compartment interjacent the deionising compartments.

7. An electrodialysis apparatus as claimed in claim 6 wherein the water to be purified is caused to allowed to flow through the deionising compartments in succession.

8. An electrodialysis apparatus as claimed in any of claims 5 to 7, characterised in that the deionising path contains ion exchange material.

9. An electrodialysis apparatus as claimed in any of claims 5 to 8, characterised in that the concentrating path contains ion exchange material.

10. An electrodialysis apparatus as claimed in any of claims 5 to 9, characterised in that said gas concentrating means comprises a plenum receptacle that is arranged to receive ion depleted water from the deionising path, and to allow the ion depleted water to stand in the plenum receptacle prior to delivery as product, so as to allow gas present in the water to collect at or towards the top of the receptacle, and said supplying means are arranged to supply the concentrating path with ion depleted water from at or towards the top of the plenum receptacle.

11. An electrodialysis apparatus substantially as hereinbefore described with reference to and as illustrated in the Figure of the accompanying drawings.

12. A method of electrodialysis as claimed in claim 1 and substantially as hereinbefore described.

The Patent Office

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Application No:	GB 9705377.1	**Examiner:**	Peter Beddoe
Claims searched:	1-12	**Date of search:**	19 May 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7B (BDSA, BDSC, BDSM, BDVA, BDVB, BDWD, BDWE, BEFX)

Int Cl (Ed.6): C02F (1/46, 1/469); B01D (61/42, 61/44, 61/46, 61/48); B01J 47/08

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0716090 A1	(ASAI) see esp fig 1 & p8 lines 38-53	5
X	WO 95/32791 A1	(NEUMEISTER) see esp fig 2	1,5
X	US 5135622	(AT & T) see esp fig 1 & col4 lines 21-44	5
X	US 4636296	(KUNZ) see esp claim 1, col7 lines 30-41 & fig 1	1,5
A	GB 815154	(PERMUTIT) see whole doc	
A	US 5589050	(AQUAMIN) see whole doc	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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